Supporting information for

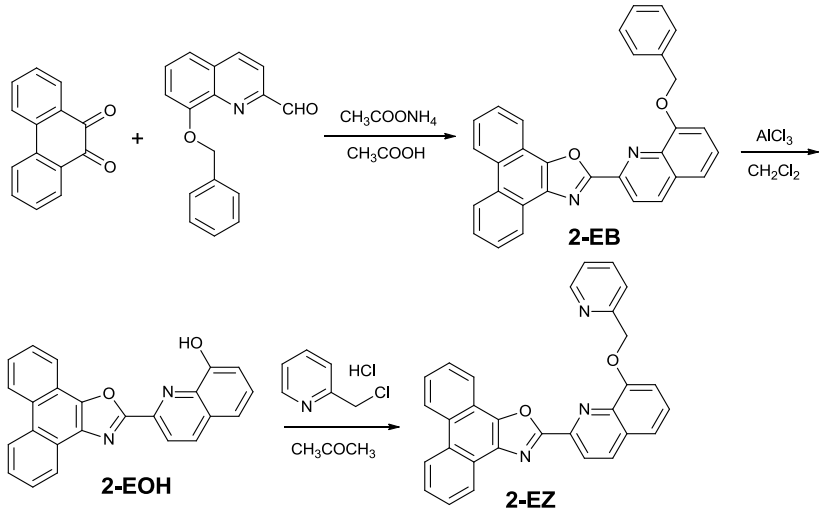
A Highly Selective Ratiometric Fluorescent Chemosensor for Cd^{2+} Ion

Li-Kun Zhang, Qing-Xiao Tong and Long-Ji Shi*

Materials and Instruments

Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. ^{1}H NMR spectra were recorded on a Bruker Avance 400 spectrometer (400 MHz) using TMS as internal standard. Mass spectra (EI and MALDI-TOF) were obtained on GCT and Autotlex III spectrometers, respectively. Steady-state emission spectra were recorded at ambient temperature on a Hitachi F-7000 Spectrophotometer and UV/Vis spectra were recorded on a Perkin-Elmer Lambda 2S UV−visible spectrophotometer.

Preparation of 2-EZ



(1) Synthesis of 2-EB

9,10-phenanthrenequinone (0.42 g, 2 mmol), 8-(benzyloxy)quinoline-2-carbaldehyde[1] (0.58 g, 2.2 mmol) and ammonium acetate (1.5 g, 20 mmol) was refluxed in glacial acetic acid (30 ml) for 12 h. After cooling to room temperature, poured it into ethanol solution under stirring. The separated solid was filtered, washed with ethanol and dried in air. The solid was purified by column chromatography on silica gel to obtain 2-EB as a pale yellow solid. Yield: 0.41 g (45.4%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ_H[ppm]: 8.76 (t, *J* = 7.6 Hz, 2H), 8.70 (dd, *J* = 7.8, 1.0 Hz, 1H), 8.63 (d, *J* = 8.6 Hz, 1H), 8.57-8.51 (m, 1H), 8.34 (d, *J* = 8.6 Hz, 1H), 7.82-7.67 (m, 6H), 7.53-7.43 (m, 4H), 7.39 (d, *J* = 7.4 Hz, 1H), 7.18 (dd, *J* = 6.0, 2.9 Hz, 1H), 5.55 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$, TMS) δ_C[ppm]: 161.15, 155.06, 146.09, 145.01, 140.59, 137.21, 137.04, 135.71, 129.96, 129.82, 129.20, 128.58, 128.15, 127.82, 127.55, 127.31, 127.18, 126.95, 126.40, 126.26, 123.70, 123.51, 123.07, 121.81, 121.18, 120.68, 120.01, 111.54, 71.37. MS(MALDI-TOF):

calcd.for $C_{31}H_{20}N_2O_2$, $[M+H]^+$453.2, found 453.3, $[M+Na]^+$475.2, found 475.3.

(2) Synthesis of 2-EOH

To a solution of 2-EB (0.23 g, 0.5 mmol) and N, N-dimethylaniline (0.40 ml, 3 mmol) in CH_2Cl_2 (20 ml) was added powdered $AlCl_3$ (0.40 g, 3 mmol) at room temperature. After stirring for 3 h, the reaction mixture was quenched by addition of 1N HCl (2 ml), and then extracted with CH_2Cl_2. The organic layer was washed with $NaHCO_3$ solution, dried over anhydrous Na_2SO_4, and the solvent was removed under reduced pressure. The remaining residue was purified by column chromatography to afford 2-EOH as a yellow solid. Yield: 0.16 g (88.9%).^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ_H[ppm]: 8.83-8.60 (m, 3H), 8.60-8.38 (m, 3H), 8.32 (d, *J* = 8.5 Hz, 1H), 7.83-7.63 (m, 4H), 7.54 (t, *J* = 7.9 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.28 (d, *J* = 7.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$, TMS) δ_C[ppm]:160.42, 152.81, 146.00, 143.71, 138.07, 137.11, 135.63, 129.97, 129.24, 129.16, 128.78, 127.61, 127.45, 127.11, 126.52, 126.07, 123.77, 123.49, 123.02, 121.50, 120.97, 120.76, 117.88, 111.08. MS(EI^+): calcd.for $C_{24}H_{14}N_2O_2$, $[M]^+$ 362, found 362.

(3) Synthesis of 2-EZ

A mixture of 2-EOH (0.18 g, 0.5 mmol), 2-chloromethyl pyridine hydrochloride (0.2 g, 1.2 mmol), K_2CO_3 (1.38 g, 10 mmol) and KI (83 mg, 0.5 mmol) in acetone (60 ml) was refluxed for 18 h. After cooling, the mixture was filtered to remove salts, and the filtrate was evaporated to generate the crude residue, which was purified by column chromatography on silica gel to obtain 2-EZ as a yellow solid. Yield: 0.15 g (65.7%). ^{1}H NMR (400 MHz, DMSO-d_6, TMS) δ_H[ppm]: 9.02 (dd, *J* = 12.8, 8.3 Hz, 2H), 8.72-8.54 (m, 4H), 8.39 (d, *J* = 7.9 Hz, 1H), 8.04-7.77 (m, 6H), 7.66 (dd, *J* = 16.9, 7.7 Hz, 2H), 7.43 (t, *J* = 8.6 Hz, 2H), 5.58 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$, TMS) δ_C[ppm]: 161.10, 157.40, 154.66, 148.98, 146.06, 145.09, 140.36, 137.04, 135.76, 129.99, 129.79, 129.19, 128.18, 127.57, 127.57, 127.27, 126.96, 126.43, 126.25, 123.77, 123.50, 123.07, 122.70, 121.67, 121.16, 120.75, 120.15, 111.09, 71.70. HRMS(EI^+), $[M]^+$ 453.1477, found 453.1247. Anal. calcd. for $C_{30}H_{19}N_3O_2$: C 79.45, H 4.22, N 9.27, O 7.06; found: C 79.35, H 4.25, N 9.31, O 7.09.

1 L. Xue, H. H. Wang, X. J. Wang and H. Jiang, *Inorg. Chem.*, 2008, **47**, 4310.

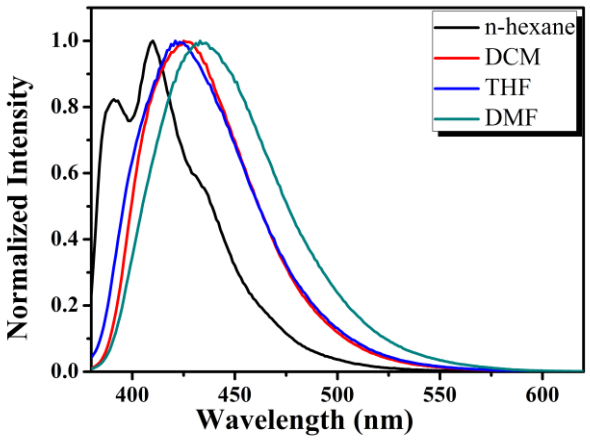


Fig. S1 Normalized fluorescence spectra of **2-EZ** (λ_{ex} = 375 nm) in different solvents.

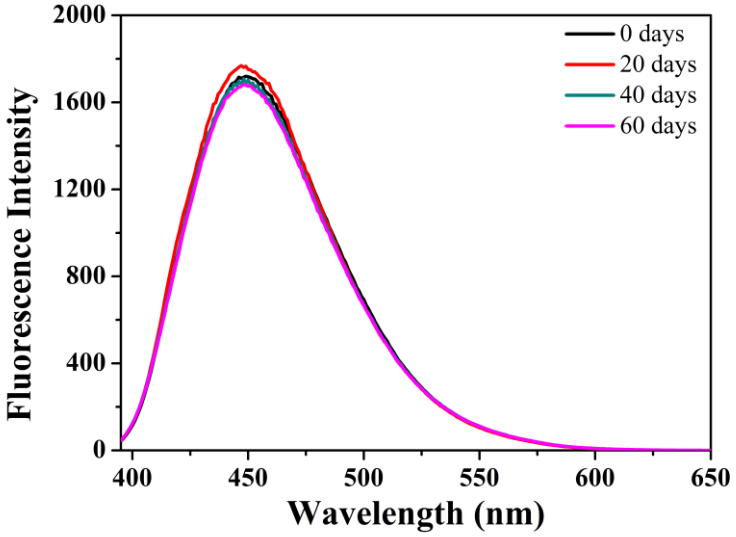


Fig. S2 Fluorescence spectra of **2-EZ** in aqueous solution ((10 mM HEPES; DMF/H_2O = 1:1, v/v; pH 7.2) kept at room temperature (25 ± 5°C). The fluorescence spectra (λ_{ex} = 375 nm) was measured after 0, 20, 40, 60 days.

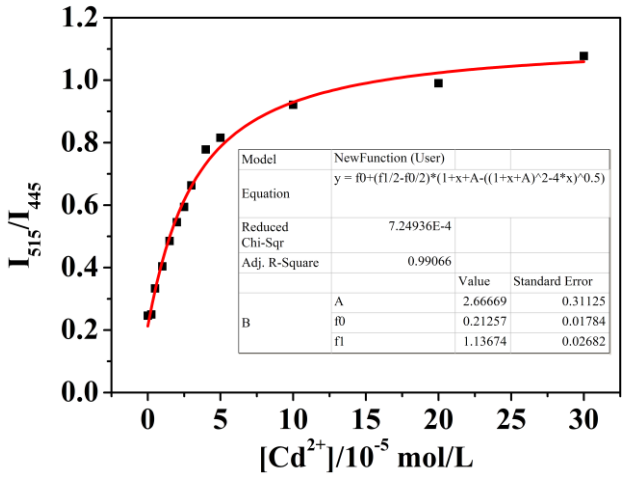


Fig. S3 A nonlinear curve fitting based on a 1:1 complex according to the equation:

$$F = F_0 + \frac{F_{max} - F_0}{2}\left\{1 + \frac{C_M}{C_L} + \frac{1}{K_S C_L} - \left[\left(1 + \frac{C_M}{C_L} + \frac{1}{K_S C_L}\right)^2 - 4\frac{C_M}{C_L}\right]^{1/2}\right\}$$

Where F and F_0 are the fluorescence intensity ratios of **2-EZ** in the presence and absence of Cd^{2+}, C_M and C_L are the concentrations of Cd^{2+} and **2-EZ**, and K_S is the stability constant.

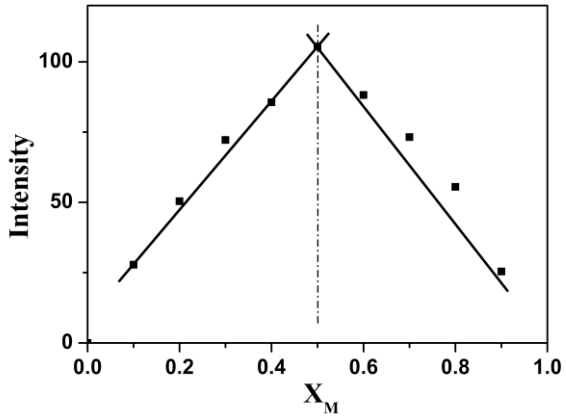


Fig. S4 The Job's plot for determining the stoichiometric ratio between **2-EZ** and Cd^{2+}, where the variations of fluorescence at 445 nm were measured as a function of molar ratio X_M ($[Cd^{2+}]/([Cd^{2+}]+[1])$).

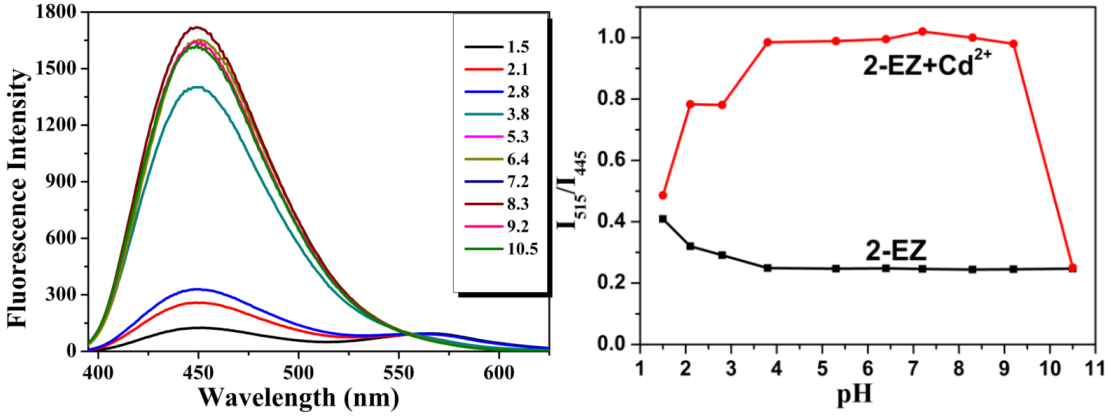


Fig. S5 Left: Fluorescent spectrum of 2-EZ at different pH. Right: Emission ratio (I_{515}/I_{445}) of 2-EZ (10 μM) vs. pH values in the absence (black line) and in the presence (red line) of Cd^{2+}. The experiment was carried out in H_2O/DMF buffer solution (50% DMF). λ_{ex} = 375 nm.

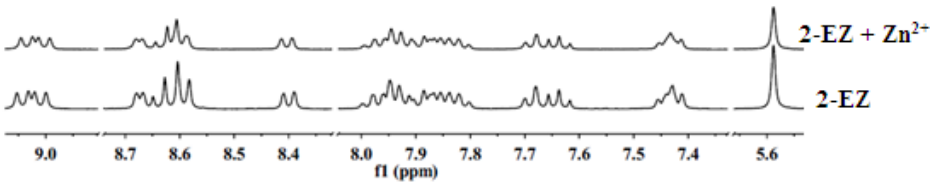


Fig. S6 ^1H NMR spectra of **2-EZ** in the absence and presence of Zn^{2+} ions in DMSO-*d6*;

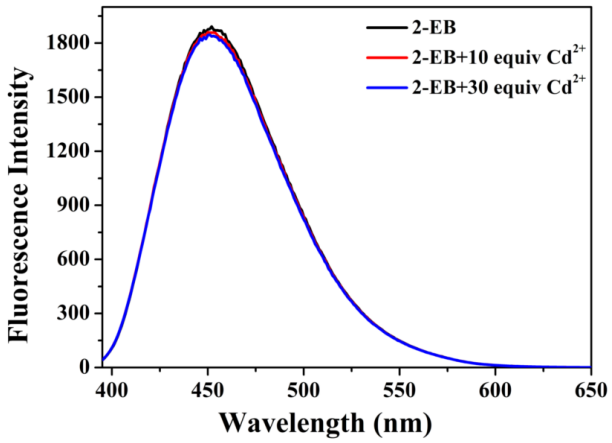


Fig. S7 Fluorescence response of **2-EB** (10 μM) in aqueous solution (10 mM HEPES; DMF/H_2O = 1: 1, v/v; pH 7.2) upon addition of Cd^{2+} (0 to 30 equiv). Excitation at λ = 375 nm.

Table S1 Photophysical properties of 2-EZ upon addition of various metal ions

Entry	λ_{em}	Quantum yield[a]	Entry	λ_{em}	Quantum yield
2-EZ	450 nm	0.978	2-EZ + Co^{2+}	449 nm	0.956
2-EZ + Na^{+}	450 nm	0.974	2-EZ + Hg^{2+}	450 nm	0.751
2-EZ + K^{+}	450 nm	0.975	2-EZ + Pb^{2+}	450 nm	0.756
2-EZ + Ca^{2+}	450 nm	0.968	2-EZ + Fe^{3+}	448 nm	0.653
2-EZ + Mg^{2+}	450 nm	0.971	2-EZ + Zn^{2+}	450 nm	0.958
2-EZ + Ag^{+}	449 nm	0.964	2-EZ + Cu^{2+}	451 nm	0.242
2-EZ + Ni^{2+}	450 nm	0.952	2-EZ + Cd^{2+}	482 nm	0.579

a. the emission quantum yield were estimated relative to quinine sulfate in 0.5 M H_2SO_4 as the standard (Φ_{em} = 0.546)